Novel vinegar-derived product enriched with dietary fiber: effect on polyphenolic profile, volatile composition and sensory analysis

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Abstract Dietary fiber derived from citrus fruits was added to vinegar. Different sources and quantities of fiber and storage conditions have been scrutinized. Formulated vinegars were evaluated on the basis of their phenolic profile, volatile composition and sensory analysis. The addition of citrus fiber enhanced the phenolic and volatile profile of the resulted vinegars. Whereas lemon fiber contributed mostly to the enrichment of the polyphenolic composition, orange fiber was that which increased in a higher way the volatile composition of the vinegars. Moreover, the content of hydroxycinnamic acid derivatives and the majority of volatile compounds decreased as the dose of fiber increased. Furthermore, the judges preferred fiber-enriched vinegars, but in different quantities depending of the fiber source. This preference was mainly based on citric attribute, contributing several terpenes and ketones derived from them. The addition of citrus fiber to vinegar did not result in a marked storage-dependence.

Keywords Vinegar · Dietary fiber · Polyphenols · Volatile compounds · Sensory analysis

Introduction

In the last few years, consumers are becoming more conscious of their nutrition and food health. In that way, the consumption of products with beneficial properties such as antioxidant, anti-inflammatory or anti-cardiovascular, and prevent certain diseases, has been on the rise.

Dietary fiber is present in a number of natural products, such as fruits, vegetables and grains. The consumption of dietary fiber is related to beneficial properties, such as the prevention of cardiovascular problems, cancer and diabetes, among other diseases (Cho and Dreher 2001). Dietary fiber derived from cereals has been widespread advertised, but increasingly, the fiber to fruit and vegetables are being introduced in the market because of its better nutrition quality (Saura-Calixto and Larrauri 1996). In that way, the determination of dietary fiber of fruits has been widely studied, and in many cases, has been correlated with the polyphenolic content and antioxidant activity. Several authors have studied the dietary fiber in the peels of orange, lemon, lime and grapefruit, (Larrauri et al. 1996; Figuerola et al. 2005; Ubando-Rivera et al. 2005). Other authors have studied the fiber in apple, (Figuerola et al. 2005) and in concentrates of mango, peach, orange and date (Grigelmo-Miguel et al. 1999; Grigelmo-Miguel and Martín-Belloso 1999; Elleuch et al. 2008; Vergara-Valencia et al. 2007). In grapes and wines, only few researches have been found, (Bravo and Saura-Calixto 1998; Deng et al. 2011; Valiente et al. 1995) and dietary fiber in several Spanish and American grape varieties was analyzed. Also other authors monitored the dietary fiber of Cencibel skins and red wines from different locations of Spain (Saura-

Highlights Novel vinegar product enriched with dietary fiber has been developed

Source and amount of fiber and storage conditions have been studied
Fiber addition modified polyphenolic and volatile profile of vinegar
Storage conditions were not significant
New products were better appreciated from a sensory point of view

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Calixto 1998; Saura-Calixto and Díaz-Rubio 2007), and in wine grape pomace (Zhu et al. 2014). However, up to date, no scientific paper in wine vinegars have been reported.

The fact that the high amounts of wine, and subsequent derived products such as vinegar, are being developed in many regions of the world, provides an opportunity for value-added product development through innovative formulas and technologies. In fact, nowadays, oenology market is turning towards diversification by means of the development of original, novel and enriched new products. Although Asian countries have a consolidate industry about these kind of products, a few researches about wine vinegars have been developed in Western countries. For instance, new Sherry vinegar-derived products based on maceration with different fruits, (Cejudo Bastante et al. 2010; Cejudo-Bastante et al. 2013) as well as fruit juices from different raw materials enriched with Sherry wine vinegar (Cejudo-Bastante et al. 2012) have been developed by our research group. However, no detailed study concerning fiber enrichment of vinegars has been performed up to now.

Following the research line of diversification of Sherry wine vinegar and improving its added value from a nutritional point of view, a new Sherry vinegar-derived product enriched with dietary fiber have been developed in the present work. Different quantities of dietary fiber were added in order to establish the best conditions of the formula. Polyphenolic composition and volatile profile of Sherry wine vinegars enriched with fiber from orange and lemon fruits were studied, and in order to check the possible acceptance by consumers, descriptive sensory analysis was also carried out. Moreover, in order to simulate the possible commercial conditions, two different storage conditions of those products were studied.

Material and methods

Samples

A Sherry wine vinegar (non aged, 7 g acetic acid/100 mL and 1 % ethanol, v/v), supplied by a local winery, was employed to carried out the present research. This vinegar was enriched with different dietary fibers from orange and lemon fruits (Indulleida, Lleida, Spain). For each type of fiber, different amounts were added to the vinegar, resulting in the following concentrations: 0.1 g/L, 0.5 g/L, 1 g/L, 5 g/L and 10 g/L (labeled as 1, 2, 3, 4 and 5, respectively). Sherry wine vinegar without the addition of dietary fiber (control vinegar, 0) was also taken into account. The vinegars were kept at different storage conditions: room temperature (25 °C) under light conditions (RT), and low temperature (4 °C) under dark conditions (LT). These temperature and luminosity conditions were chosen in order to reflect as much as possible different

commercial terms. Samples were also monitored after 2 months of the fiber addition.

Analysis of polyphenols and furanic compounds

A Water Acquity UPLC system was used for the separation, identification and quantification of phenolic compounds, equipped with a diode array detector (DAD), according to the method proposed by Schwarz et al. (2009). An Acquity UPLC BEH C18 column (100×2.1 mm/ID, with 1.7 µm particle size), also from Waters, was used. The identification of each compound was carried out by comparing retention times and UV–vis spectra with those provided for commercial standards. When commercial standards were not available, the calibration curves of compounds with similar chemical structures were employed. All the analyses were carried out in duplicate.

Several phenolic compounds (such as benzoic acids, hydroxycinnamic acid derivatives and glycosilated flavanones) and furanic derivatives were identified. DAD chromatograms obtained at 280 nm were used for the identification and quantification of benzoic acids, furanic derivatives and glycosilated flavanones, whereas a wavelength of 320 nm was used for the hydroxycinnamic acid derivatives. Individual standards were used for each benzoic acid, furanic derivative and glycosilated flavanone, whereas caffeic and *p*-coumaric acids were employed for the respective hydroxycinnamic acid derivatives, and hesperidin was used as standard of neohesperidin.

Analysis of volatile compounds

10 mm×0.5 mm (length×film thickness) PDMS commercial stir bars, supplied by Gerstel (Mülheim a/d Ruhr, Germany) were used for the extractions. For each SBSE analysis, a volume of 25 mL of sample was pipetted and placed into a 100 mL Erlenmeyer flask with 5.85 g of NaCl (Scharlau, Barcelona, Spain) and 84 µL of a solution of 4-methyl-2-pentanol, internal standard, (Sigma, Steinheim, Germany) (2.27 g/L in Milli-Q water containing 80 g/L of acetic acid), according to the method proposed by Cejudo Bastante et al. (2010).

A commercial TDS-2 thermal desorption unit (Gerstel) connected to a programmed-temperature vaporization (PTV) injector CIS-4 (Gerstel) by a heated transfer line were used for the thermal desorption of the coated stir bars. The PTV was installed in an Agilent 6890 GC-5973 MS system (Agilent Technologies, Palo Alto, CA, USA). An empty baffled liner was used in the PTV. The thermodesorption unit was equipped with a MPS 2 L autosampler (Gerstel) capable of handling the program for 98 coated stir bars. An Agilent 6890 GC-5973 N MS system (Agilent, Little Falls, DE, USA), equipped with a DB-Wax capillary column (J&W Scientific, Folsom, CA, USA), 60×0.25 mm I.D., with a 0.25 µm coating were used

in order to perform the capillary GC-MS analysis in the electron impact mode.

Peak identification was carried out using the Wiley library (Wiley Registry of Mass Spectral Data, 7th Edition, 2000) by analogy of mass spectra and confirmed by retention times of standards when they were available or by the retention data from the literature. For a large extent of compounds, the retention indices were determined (on a DB-Wax polar column) in a previous study (Cejudo-Bastante et al. 2013) and compared with those from literature. Semi-quantitative data were obtained by measuring the relative molecular ion peak area in relation to that of 4-methyl-2-pentanol, the internal standard.

Sensory analysis

Sherry wine vinegars with and without the addition of dietary fiber were tested by a group of 12 to 15 expert assessors, with a medium/high experience in sensory analysis of vinegars. Assessment took place in a standard testing room, (ISO 2007) equipped with separated booths and olive oil testing glasses (ISO 2006b) in order to avoid the influence of the vinegar sample color. As well, glasses were covered with a watch-glass to minimize the escape of volatile substances. In each booth, lettuce leaves were supplied as the vehicle for gustatory analysis. Room temperature was fixed at 22 °C. The panel judges, belonging all of them to laboratory personnel, were submitted to a validation study, in which judgment repeatability and the panel homogeneity were evaluated. Duplicated discrimination test and descriptive profile of 2 reference samples were employed to validate the judges' reproducibility; whereas for each descriptor, a two factor ANOVA (judges x samples) of the descriptive data allowed to study the homogeneity of the panel. The panelists carried out two different types of tests. Quantification of several analytical descriptors were carried out by using interval scales in all the cases. (ISO 2003) Prior to descriptive profiling, a stage for generating appropriate descriptors to define the samples was carried out. In addition, samples were submitted to ranking test (ISO 2006a) with the aim of ordering samples according to assessor's preference. These two evaluations were carried out at different sessions. All vinegar samples were evaluated by orthonasal way in duplicate.

Statistical analysis

The complete set of analytical data was submitted to analysis of variance (ANOVA), correlation assays, cluster analysis, and linear discriminant analysis (LDA) using the statistical computer packages Statgraphics Centurion, version 15.0 (Statpoint Inc., USA), and SPSS Statistics version 17.0 (IBM Corp. NY, USA) for Windows XP. Quantitative sensory data were analyzed by ANOVA test, and ranking data by

preference were submitted to Friedman test, as ISO 8587 standard specifies.

Results and discussion

Polyphenolic compounds

Thirteen polyphenolic compounds have been determined in the different fiber-enriched vinegars, and their concentrations are presented in Table 1. In parallel, vinegar without fiber addition (control vinegar) has also been conducted to highlight possible differences among the samples.

The well-described polyphenolic compounds from Sherry vinegar (furanic derivatives, benzoic acids and hydroxycinnamic acid derivatives) were determined (e.g., gallic acid, protocatechuic acid, *p*-hydroxybenzaldehyde, caffeic acid, etc.), and with concentration levels similar to those found in the literature (Alonso et al. 2004; Jayaprakasha and Patil 2007). In addition, new compounds (glycosilated flavanones: narirutin, naringin, hesperidin and neohesperidin), not found in the control Sherry vinegar, were also identified.

In order to statistically highlight the differences in the polyphenolic content among the samples, data were submitted to ANOVA, considering the effect of three factors: type of product, amount of fiber and storage conditions. As can be seen, these three factors were significant ($p < 0.05$) for most of the polyphenols studied (Table 1). As can be seen, the typically identified polyphenols in control vinegars were also identified in fiber-enriched samples, and even at higher concentrations. Glycosilated flavanones were transferred to control vinegars after fiber addition. In a study about the use of natural sweeteners as sucrose alternatives of chocolate, (Belščak-Cvitanović et al. 2015) a bioactive profile enrichment was also occurred due to the presence of phenolic acids, flavone and flavonol derivatives, which were not identified in control chocolate. In general terms, fiber from lemon enriched the polyphenolic profile of Sherry vinegars in a significantly higher way than that from orange (ANOVA "type" factor). Specifically HMF, protocatechuic acid, tyrosol, *p*-hydroxybenzaldehyde, *trans-p*-caftaric acid, *trans-p*-coutaric acid and caffeic acid were found in higher concentrations in vinegars with lemon fiber. Regarding glycosilated flavanones, narirutin was detected in all enriched samples stored at low temperature/dark conditions (LT), whereas for the samples stored under room temperature and the influence of the light (RT), only those submitted to the highest amounts of fiber (L3RT, L4RT, L5RT for lemon; and O4RT and O5RT for orange) presented this compound. Naringin seemed to be exclusive of the orange fiber, and neohesperidin appeared only when the content of orange fiber increased (O4LT, O5LT, O4RT and O5RT). Moreover, hesperidin was the main glycosilated flavanone detected in the fiber-enriched vinegars, regardless of the origin. These results are in

Table 1 Mean values (mg/L) of polyphenols for the enriched vinegar with lemon (L) and orange (O) fibers and control vinegar (C) after storage at room temperature/light conditions (RT) and at low temperature/dark conditions (LT) for the five increasing quantities of added fiber (0, 1, 2, 3, 4, 5), and analysis of variance (ANOVA). Relative standard deviations < 10 %

Samples	Polyphenols													
	Furanic derivative		Benzoic acids			Glycosylated flavanones					Hydroxycinnamic acid derivatives			
	HMF		gallic acid	protocatechuic acid	tyrosol	<i>p</i> -OH-benzaldehyde	narirutin	naringin	hesperidin	neohesperidin	<i>t</i> -caftaric acid	<i>t</i> - <i>p</i> -coumaric acid	<i>c</i> - <i>p</i> -coumaric acid	caffeic acid
C0LT	13.94		15.45	25.86	24.08	3.20	nd	nd	nd	nd	16.61	3.93	1.33	3.16
C0RT	14.80		14.17	27.01	23.93	4.49	nd	nd	nd	nd	12.47	8.92	4.49	7.30
L1LT	15.71		12.31	27.66	30.32	4.50	17.87	nd	nd	nd	19.20	15.16	1.79	9.05
L2LT	15.67		12.63	27.77	27.77	3.90	18.65	nd	nd	nd	18.16	14.79	3.01	8.12
L3LT	16.29		12.41	27.98	32.97	3.23	10.28	nd	nd	nd	17.66	10.74	3.02	3.64
L4LT	20.87		13.25	27.88	38.06	3.80	15.63	nd	14.41	nd	15.23	12.36	2.93	6.10
L5LT	26.34		14.42	29.89	48.75	3.11	15.40	nd	12.38	nd	17.31	13.20	3.03	7.10
L1RT	14.76		12.42	26.12	10.39	4.41	nd	nd	17.25	nd	12.22	7.97	5.25	6.65
L2RT	15.40		12.00	27.21	10.32	4.45	nd	nd	19.36	nd	12.63	8.08	5.19	6.67
L3RT	16.15		12.39	27.56	10.15	4.48	16.99	nd	21.91	nd	12.61	7.99	5.14	6.47
L4RT	21.76		13.40	32.42	10.35	4.65	25.74	nd	45.45	nd	12.45	7.73	4.26	3.24
L5RT	28.50		14.89	38.34	10.22	4.61	26.30	nd	73.86	nd	12.61	7.34	4.40	6.20
O1LT	15.11		12.85	27.79	9.74	2.06	11.05	12.22	19.60	nd	17.75	10.90	4.35	8.05
O2LT	14.66		14.21	27.82	9.26	1.11	10.66	14.89	30.18	nd	18.10	10.26	4.24	5.14
O3LT	14.20		15.06	25.26	8.63	1.31	15.96	15.01	34.04	nd	17.36	9.29	4.15	4.94
O4LT	14.40		13.89	25.73	10.29	0.61	9.73	15.50	74.00	8.40	14.17	7.93	3.98	5.88
O5LT	14.81		7.78	24.91	11.36	1.39	10.42	14.71	94.93	12.23	10.28	5.43	2.79	4.75
O1RT	14.59		14.38	26.45	9.75	4.59	nd	10.53	21.29	nd	14.42	9.23	4.04	3.09
O2RT	14.68		14.41	26.18	9.88	4.47	nd	11.64	32.14	nd	14.39	9.13	3.98	3.07
O3RT	14.70		14.15	26.44	9.80	3.81	nd	13.99	37.14	nd	13.44	8.76	2.18	3.09
O4RT	16.64		14.22	28.44	10.58	3.24	10.21	13.64	75.07	8.99	12.46	7.95	3.68	6.28
O5RT	18.55		13.70	29.21	12.32	4.52	12.11	15.06	100.99	13.50	10.42	6.48	3.00	5.27
ANOVA														
Type	0.0000*		0.1092	0.0000*	0.0000*	0.0000*	0.0000*	0.0000*	0.0000*	0.0000*	0.5965	0.0000*	0.4968	0.0044*
Amount	0.0000*		0.1120	0.0000*	0.0018*	0.0030*	0.0001*	0.0000*	0.0000*	0.0000*	0.0026*	0.0000*	0.3136	0.0599
Storage	0.0000*		0.0180	0.0000*	0.0000*	0.0000*	0.0010*	0.0001*	0.0000*	0.0066*	0.0000*	0.0000*	0.0029*	0.0073*

*Values are statistically significant at $p < 0.05$

nd compound not detected

agreement with those obtained in a previous work (Cejudo Bastante et al. 2010) about Sherry vinegars macerated with different fruits, and also with other authors who studied the phenolic composition of lemon and orange (Grandi et al. 1994; Kelebek et al. 2009).

With regard to the doses of fiber (ANOVA “amount” factor), the content of the majority of polyphenolic compounds significantly increased as the quantity of fiber increased, mainly hesperidin, which reached 4- or 5-fold higher values in all experiences. This fact was also observed for HMF, protocatechuic acid and narirutin in lemon fiber-enriched vinegars (enhancement around 40–50 %) when they were stored under room temperature/light conditions. Surprisingly, some of polyphenolic compounds (mainly hydroxycinnamic acid derivatives) identified in orange fiber-enriched vinegars and stored under low temperature/dark conditions showed an important decrease of concentration (around 50–60 %; $p < 0.05$). Moreover, temperature and light exerted a significant effect on almost all phenolic compounds (ANOVA “storage” factor). In general, the refrigeration/dark conditions of storage provoked the maintenance of the concentration of the majority of individual polyphenolic compounds, observing a remarkable decrease when submitting samples to room temperature/light conditions. These results were in agreement with those obtained by Cejudo-Bastante et al. (2011). In this work the content of some benzoic acids (gallic acid) and hydroxycinnamic acid derivatives (*p*-coumaric and ferulic acids) found for Chardonnay white wines decreased as a consequence of the illumination storage. Taking into account the joint effect of illumination and temperature of storage, scarcely reported in bibliography, Ferreira-Lima et al. (2013) found that some phenolic compounds such as *trans*-caftaric acid and (+)-catechin decreased under room temperature/light conditions, indicating that controlled conditions of storage reduce the degradation and oxidation reactions that occur in wines during aging. Other authors (Recamales et al. 2006) established that factors such as light and temperature might contribute to the degradation of some individual phenolic compounds such (+)-catechin and *trans*-caftaric acid, attributed to oxidation and polymerization phenomena. Among them, hesperidin and *p*-OH-benzaldehyde were the phenolic compounds that most contributed to that differentiation. However, some phenolic compounds manifested the opposite effect, i.e., the higher amounts of polyphenols were observed for those samples stored at room temperature and light conditions. That is the case of *p*-hydroxybenzaldehyde, mainly due to the low values observed in orange fiber-enriched vinegars under refrigeration/dark conditions. This fact could be due to possible precipitation as a consequence of the low temperature.

Volatile composition

In this research work, a total of 60 individual volatile compounds were identified in the different vinegars, belonging to

different chemical families: esters and acetates, alcohols, acids, terpenes, benzenic compounds, furanic compounds, lactones, and aldehydes and ketones. Table 2 shows the mean relative area values (quantifying ion peak area / internal standard molecular ion peak area) for each sample.

In order to better understand the behaviour of the main volatile compounds according to the treatment applied, data were submitted to ANOVA (Table 3). For that purpose, similarly to that carried out for polyphenols, three independent factors (type of product, amount of fibre and storage conditions) were taken into account. In general, the factors that mostly influenced the differentiation among samples were “type” and “amount” of fiber, whereas the “storage” factor exerted a lower effect on the volatile profile changes. In general terms, all the vinegars enriched with fiber increased their individual volatile compound concentrations (ANOVA “type” factor). Fiber from orange was the raw material that significantly improved the volatile profile, contrarily to that observed for polyphenolic compounds (Tables 1 and 2). The main volatile compounds that contributed to the differentiation according to the type of sample were benzenic compounds (eugenol and some phenols), followed by acetates (benzyl, 2-ethylphenyl and 2-phenyl acetates), short- and medium-chain acids (isovaleric, isobutyric and hexanoic acids) and alcohols (2-methyl-butanol) and some ketones derived from terpenes (neryl acetone and *cis*-geranyl acetone). All these compounds exhibited a significantly higher content in vinegars enriched with orange fiber, except for eugenol and ethyl acetate, that were more abundant in control Sherry vinegars. Furthermore, the volatile compounds associated with the differentiation according to the amount of the fiber were mainly acids (octanoic and decanoic acids), benzenic compounds, ketones and terpenes (neronidol and its ketone derivative) (ANOVA “amount” factor). Surprisingly, their content decreased as the amount of fiber increased. This fact could be due to (i) adsorption phenomena or (ii) saturation of the medium and subsequent insolubility of the fiber in the vinegar. Moreover, although temperature and light exerted a minor influence on the concentration differences among samples, some acetates (benzyl and isobutyl acetates), short- and medium-chain acids, benzaldehyde, α -terpineol, furfural and vitispirane were the main participants in the discrimination (ANOVA “storage” factor). All of them, except for vitispirane, showed a significantly higher content when samples underwent the storage at room temperature in light conditions. Benítez et al. (2003) obtained increases in the volatile composition during storage of wines exposed to the influence of the UV–vis radiation. Similar results were obtained by Marais (1986), who affirmed that the formation of furfural was accelerated when South African *Vitis vinifera* L. cv. Colombard wines were stored under the same conditions, and also by Cejudo-Bastante et al. (2011) who studied Chardonnay wines stored under light and dark conditions. Moreover, other

Table 2 Mean relative areas of volatile compounds for the enriched vinegars with lemon (L) and orange fiber (O) after storage at room temperature/light conditions (RT) and at low temperature/dark conditions (LT) for the five increasing quantities of added fiber (0, 1, 2, 3, 4, 5). Relative standard deviations <15 %

Room temperature / Light conditions (RT)												
	Control vinegar (C)		Lemon fiber (L)					Orange fiber (O)				
	C0RT	L1RT	L2RT	L3T	L4T	L5RT	O1RT	O2RT	O3RT	O4RT	O5RT	
<i>Esters and acetates</i>												
β-phenyl propanoic acid ethyl ester	0.029	0.027	0.027	0.025	0.026	0.021	0.025	0.032	0.034	0.023	0.020	
hexanoic acid ethyl ester	0.010	0.030	0.022	0.026	0.031	0.019	0.016	0.026	0.019	0.016	0.021	
decanoic acid ethyl ester	0.078	0.050	0.034	0.074	0.057	0.060	0.036	0.037	0.047	0.040	0.099	
benzyl acetate	0.048	0.050	0.053	0.045	0.051	0.046	0.053	0.062	0.065	0.053	0.052	
methyl salicylate	0.015	0.016	0.016	0.014	0.015	0.013	0.015	0.018	0.019	0.015	0.015	
2-ethyl phenyl acetate	0.184	0.189	0.193	0.169	0.187	0.168	0.186	0.222	0.234	0.186	0.188	
2-phenyl acetate	2.828	2.765	2.819	2.627	2.983	2.722	2.764	3.524	3.726	3.179	3.150	
isobutyl acetate	1.567	1.485	1.715	1.559	1.692	1.482	1.481	1.680	1.788	1.582	1.663	
ethyl isovalerate	0.445	0.483	0.484	0.440	0.475	0.399	0.322	0.352	0.379	0.323	0.441	
isoamyl acetate	3.594	3.688	4.206	3.305	4.075	3.754	3.267	4.139	4.080	4.405	4.162	
ethyl acetate	5.797	5.925	6.269	5.553	6.282	5.645	5.600	6.836	7.238	6.425	6.471	
<i>Alcohols</i>												
1-(2-methoxyphenyl) ethanol	0.169	0.170	0.184	0.147	0.177	0.156	0.189	0.216	0.234	0.181	0.182	
2-methyl-1-butanol	2.197	2.556	2.271	1.955	2.251	2.102	2.065	2.510	2.474	3.153	2.744	
2-phenyl alcohol	0.681	0.718	0.736	0.640	0.708	0.664	0.715	0.856	0.890	0.765	0.709	
isoamyl alcohol	0.237	0.236	0.253	0.221	0.242	0.222	0.229	0.260	0.266	0.248	0.228	
<i>Acids</i>												
butanoic acid	0.030	0.025	0.028	0.024	0.030	0.028	0.025	0.039	0.032	0.030	0.024	
2-phenyl propanoic acid	0.029	0.027	0.027	0.025	0.026	0.021	0.025	0.032	0.034	0.023	0.020	
isobutyric acid	0.218	0.136	0.306	0.233	0.262	0.235	0.272	0.315	0.314	0.269	0.236	
isovaleric acid	1.501	1.754	1.731	1.528	1.760	1.552	1.602	2.019	2.052	1.766	1.725	
hexanoic acid	0.200	0.212	0.221	0.180	0.207	0.194	0.205	0.246	0.241	0.202	0.191	
heptanoic acid	0.026	0.030	0.017	0.016	0.020	0.022	0.016	0.023	0.022	0.021	0.021	
octanoic acid	1.101	1.212	1.127	0.983	1.077	0.931	1.089	1.338	1.356	1.049	0.964	
nonanoic acid	0.997	1.126	1.067	0.858	0.882	0.696	1.067	1.219	1.229	0.871	0.853	
decanoic acid	0.807	0.877	0.710	0.577	0.455	0.277	0.677	0.819	0.801	0.386	0.296	
dodecanoic acid	0.075	0.108	0.057	0.039	0.029	0.022	0.060	0.051	0.057	0.037	0.082	
<i>Terpenes</i>												
β-terpineol	0.002	nd	nd	nd	nd	0.003	nd	0.003	0.002	0.008	0.014	
valencene	0.004	0.002	0.002	0.001	0.001	0.002	0.002	0.001	0.001	0.009	0.017	

Table 2 (continued)

	Room temperature / Light conditions (RT)									
	Control vinegar (C)			Lemon fiber (L)			Orange fiber (O)			
	C0RT	L1RT	L2RT	L3T	L4T	L5RT	O1RT	O2RT	O3RT	O5RT
neronidol	0.145	0.149	0.149	0.127	0.136	0.115	0.142	0.173	0.174	0.128
citronellol	0.001	nd	nd	0.001	tr	0.001	0.001	0.001	0.001	tr
<i>cis</i> -limonene oxide	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
eucalyptol	1.871	0.717	0.108	0.133	0.146	nd	nd	2.015	nd	0.535
4-terpineol	0.058	0.003	0.002	0.021	0.007	0.030	0.002	0.003	0.005	0.014
α -terpineol	0.030	0.005	0.008	0.030	0.062	0.114	0.008	0.028	0.063	0.335
<i>Benzenic compounds</i>										
eugenol	0.051	0.027	0.029	0.037	0.031	0.035	0.028	0.030	0.038	0.019
2-ethyl phenol	0.270	0.305	0.309	0.245	0.274	0.234	0.291	0.332	0.343	0.249
4-methyl-2,6-di- <i>tert</i> -butylphenol	0.012	0.008	0.006	0.004	0.003	0.001	0.007	0.008	0.008	0.001
4-nonyl phenol	0.010	0.009	0.005	0.003	0.002	0.001	0.006	0.005	0.004	0.001
benzaldehyde	0.166	0.198	0.229	0.189	0.206	0.187	0.196	0.218	0.224	0.197
phenol	0.018	0.026	0.019	0.016	0.017	0.016	0.015	0.018	0.021	0.018
<i>p</i> -ethyl guaiacol	0.169	0.170	0.184	0.147	0.177	0.156	0.188	0.216	0.234	0.181
4-ethyl phenol	0.270	0.305	0.309	0.245	0.274	0.234	0.290	0.332	0.343	0.260
<i>o</i> - <i>tert</i> -butyl phenol	0.402	0.045	0.022	0.026	0.016	0.086	0.020	0.022	0.022	0.008
2,4-bis(dimethylethyl) phenol	2.606	2.376	1.898	1.723	1.424	1.033	1.791	2.028	2.175	0.727
<i>Furanic compounds</i>										
furfural	0.022	0.040	0.041	0.030	0.032	0.033	0.033	0.036	0.037	0.029
<i>Lactones</i>										
δ -nonyl valerolactone	0.015	0.014	0.014	0.011	0.011	0.009	0.013	0.015	0.016	0.008
<i>Aldehydes and ketones</i>										
neryl acetone	0.015	0.010	0.008	0.018	0.026	0.030	0.006	0.013	0.020	0.058
1-(2,3,6-triethylphenyl)- butanone	0.019	0.018	0.018	0.016	0.016	0.013	0.017	0.021	0.022	0.011
mesityl oxide	0.033	0.039	0.037	0.028	0.030	0.027	0.033	0.036	0.041	0.027
2-nonanone	0.010	0.009	0.008	0.010	0.010	0.008	0.007	0.009	0.009	0.008
camphor	tr	0.213	nd	nd	1.040	0.724	nd	nd	nd	nd
(+)-carvone	0.004	0.002	0.002	0.002	0.001	0.003	0.002	0.001	0.001	0.017
<i>cis</i> -geranyl acetone	0.015	0.033	0.008	0.018	0.026	0.030	0.006	0.013	0.022	0.058
2-phenyl-2-butenal	0.005	0.005	0.005	0.005	0.006	0.006	0.006	0.007	0.007	0.006
1-(2,3,6-trimethylphenyl)-2-butanone	0.019	0.018	0.018	0.016	0.016	0.013	0.017	0.021	0.022	0.011
2,6-dimethyl-4-heptanone	0.063	0.073	0.077	0.075	0.069	0.055	0.055	0.064	0.072	0.063

Table 2 (continued)

Room temperature / Light conditions (RT)										
Control vinegar (C)	Lemon fiber (L)					Orange fiber (O)				
	L1RT	L2RT	L3T	L4T	L5RT	O1RT	O2RT	O3RT	O4RT	O5RT
C0RT										
<i>Miscellaneous</i>										
benzaldehyde α -ethylene	0.005	0.005	0.005	0.006	0.006	0.006	0.007	0.007	0.006	0.006
4-butyl butan-4-olide	0.019	0.017	0.014	0.015	0.014	0.017	0.018	0.022	0.015	0.016
acetomisoile	0.002	0.000	0.006	0.004	0.002	tr	0.001	0.003	0.005	0.009
vitispirane	0.029	0.025	0.027	0.028	0.022	0.017	0.024	0.026	0.018	0.027
<i>n</i> -butyl benzene sulfonamide	0.115	0.180	0.101	0.137	0.119	0.196	0.160	0.318	0.136	0.132
Low Temperature / Dark conditions (LT)										
Control Vinegar (C)	Lemon fiber (L)					Orange fiber (O)				
	L1LT	L2LT	L3LT	L4LT	L5LT	O1LT	O2LT	O3LT	O4LT	O5LT
C0LT										
<i>Esters and acetates</i>										
β -phenyl propanoic acid ethyl ester	0.025	0.028	0.029	0.028	0.025	0.020	0.028	0.026	0.023	0.017
hexanoic acid ethyl ester	0.023	0.023	0.020	0.001	0.027	0.010	0.011	0.016	0.021	0.052
decanoic acid ethyl ester	0.094	0.050	0.020	0.077	0.080	0.019	0.039	0.034	0.177	0.392
benzyl acetate	0.039	0.046	0.049	0.045	0.046	0.042	0.051	0.049	0.053	0.047
methyl salicylate	0.012	0.014	0.016	0.014	0.014	0.013	0.016	0.015	0.016	0.014
2-ethyl phenyl acetate	0.153	0.190	0.192	0.186	0.182	0.165	0.200	0.187	0.201	0.178
2-phenyl acetate	2.537	2.854	2.994	2.923	2.975	2.860	3.061	2.901	3.046	3.049
isobutyl acetate	1.189	1.203	1.336	1.346	1.510	1.441	1.480	1.435	1.476	1.349
ethyl isovalerate	0.431	0.348	0.388	0.402	0.449	0.411	0.428	0.416	0.434	0.383
isoamyl acetate	3.792	3.217	3.766	3.854	3.451	3.756	3.862	3.765	3.621	3.623
ethyl acetate	16.089	5.065	5.486	5.493	6.052	5.838	5.975	5.635	5.730	5.482
<i>Alcohols</i>										
1-(2-methoxyphenyl) ethanol	0.200	0.196	0.204	0.183	0.190	0.174	0.205	0.189	0.216	0.194
2-methyl-1-butanol	2.484	2.242	2.103	2.371	2.478	2.593	2.117	2.445	3.609	4.069
2-phenyl alcohol	0.597	0.748	0.723	0.756	0.704	0.647	0.727	0.698	0.754	0.715
isoamyl alcohol	0.228	0.222	0.245	0.230	0.270	0.237	0.234	0.242	0.242	0.228
<i>Acids</i>										
butanoic acid	0.027	0.008	0.028	0.024	0.026	0.023	0.024	0.028	0.025	0.013
2-phenyl propanoic acid	0.025	0.028	0.029	0.028	0.025	0.020	0.029	0.028	0.023	0.017

Table 2 (continued)

Low Temperature / Dark conditions (LT)											
	Control Vinegar (C)	Lemon fiber (L)					Orange fiber (O)				
		C0LT	L1LT	L2LT	L3LT	L4LT	L5LT	O1LT	O2LT	O3LT	O4LT
isobutyric acid	0.206	0.127	0.190	0.163	0.181	0.188	0.225	0.226	0.236	0.235	0.204
iso valeric acid	1.395	1.086	1.476	1.206	1.428	1.439	1.618	1.611	1.556	1.644	1.450
hexanoic acid	0.153	0.154	0.196	0.164	0.173	0.169	0.200	0.201	0.196	0.222	0.171
heptanoic acid	0.027	0.019	0.025	0.022	0.021	0.024	0.023	0.025	0.022	0.025	0.021
octanoic acid	1.011	1.181	1.226	1.153	1.088	0.958	1.174	1.151	1.111	1.183	0.997
nonanoic acid	0.798	1.044	1.108	0.965	0.843	0.729	1.075	1.001	0.959	0.979	0.777
decanoic acid	0.865	0.937	0.962	0.787	0.479	0.274	0.855	0.800	0.693	0.503	0.390
dodecanoic acid	0.081	0.088	0.091	0.045	0.028	0.024	0.066	0.051	0.042	0.261	0.317
Terpenes											
β-terpineol	0.002	0.002	0.002	0.003	0.003	0.002	nd	0.002	0.002	nd	0.002
valencene	0.004	0.003	0.003	0.002	0.001	tr	0.003	0.001	0.001	0.005	0.011
neronidol	0.145	0.156	0.160	0.150	0.136	0.114	0.154	0.150	0.145	0.152	0.123
citronellol	0.001	0.001	0.001	0.001	0.001	tr	0.001	0.001	0.001	tr	tr
cis-limonene oxide	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.097
eucalyptol	nd	2.189	1.926	2.405	nd	nd	nd	nd	nd	0.072	2.171
4-terpineol	0.014	0.019	0.002	0.012	0.011	0.004	0.006	0.005	0.003	0.009	0.016
α-terpineol	0.006	0.017	0.005	0.016	0.036	0.054	0.007	0.009	0.012	0.032	0.032
Benzenic compounds											
eugenol	0.036	0.030	0.030	0.040	0.034	0.026	0.031	0.025	0.020	0.024	0.026
2-ethyl phenol	0.210	0.289	0.285	0.256	0.248	0.225	0.290	0.268	0.267	0.295	0.263
4-methyl-2,6-di-tert-butylphenol	0.017	0.012	0.013	0.005	0.002	0.002	0.018	0.010	0.006	0.003	0.002
4-nonyl phenol	0.011	0.009	0.008	0.004	0.002	0.001	0.008	0.005	0.003	0.001	0.001
benzaldehyde	0.110	0.148	0.154	0.114	0.152	0.136	0.170	0.160	0.168	0.172	0.159
phenol	0.059	0.022	0.021	0.019	0.016	0.018	0.016	0.017	0.016	0.021	0.030
p-ethyl guaiacol	0.200	0.196	0.204	0.183	0.190	0.174	0.205	0.189	0.194	0.216	0.194
4-ethyl phenol	0.220	0.289	0.285	0.256	0.248	0.225	0.290	0.268	0.267	0.295	0.262
o-tert-butyl phenol	0.029	0.025	0.026	0.032	0.033	0.014	0.028	0.021	0.018	0.015	0.021
2,4-bis(dimethylethyl) phenol	3.164	2.688	2.792	2.182	1.559	1.178	2.631	2.183	1.667	1.048	0.695
Furanic compounds											
furfural	0.024	0.024	0.023	0.022	0.022	0.022	0.023	0.021	0.024	0.027	0.024
Lactones											
δ-nonyl valerolactone	0.013	0.015	0.017	0.015	0.011	0.008	0.014	0.013	0.013	0.011	0.007

Table 2 (continued)

Low Temperature / Dark conditions (LT)										
	Control Vinegar (C)	Lemon fiber (L)			Orange fiber (O)					
		L1LT	L2LT	L3LT	L4LT	L5LT	O1LT	O2LT	O3LT	
	C0LT									
<i>Aldehydes and ketones</i>										
neryl acetone	0.019	0.013	0.012	0.019	0.021	0.010	0.012	0.021	0.029	0.080
1-(2,3,6-triethylphenyl)- butanone	0.017	0.022	0.022	0.020	0.017	0.013	0.021	0.019	0.018	0.011
mesityl oxide	0.025	0.036	0.040	0.034	0.029	0.025	0.033	0.030	0.032	0.023
2-nonanone	0.010	0.009	0.007	0.008	0.009	0.007	0.009	0.008	0.008	0.007
camphor	0.489	nd	nd	nd	nd	nd	nd	nd	nd	nd
(+)-carvone	0.004	0.003	0.003	0.001	0.001	tr	0.003	0.001	0.001	0.011
cis-geranyl acetone	0.019	0.016	0.012	0.019	0.016	0.010	0.012	0.021	0.029	0.080
2-phenyl-2-butenal	0.005	0.006	0.006	0.006	0.006	0.005	0.006	0.006	0.006	0.006
1-(2,3,6-trimethylphenyl)-2-butanone	0.021	0.022	0.022	0.020	0.017	0.013	0.021	0.019	0.018	0.011
2,6-dimethyl-4-heptanone	0.055	0.062	0.073	0.061	0.059	0.059	0.062	0.071	0.067	0.051
<i>Miscellaneous</i>										
benzaldehyde α -ethylene	0.005	0.006	0.006	0.006	0.006	0.005	0.006	0.006	0.006	0.006
4-butyl butan-4-olide	0.015	0.015	0.019	0.019	0.016	0.016	0.017	0.016	0.017	0.014
acetoneisole	0.003	0.008	0.004	0.003	0.002	0.003	0.001	0.002	0.002	0.010
vitispirane	0.037	0.035	0.047	0.047	0.038	0.024	0.037	0.039	0.034	0.036
<i>n</i> -butyl benzene sulfonamide	0.939	0.105	0.141	0.224	0.148	0.123	0.129	0.129	0.110	0.307

nd compound not detected, tr trace level

authors (Marrufo-Curtido et al. 2012; Chinnici et al. 2009; Piva et al. 2008) found that furfural and other furanic compounds were more abundant in vinegars derived from a thermal treatment (traditional balsamic vinegar of Modena).

Multivariate study

With the aim of scrutinizing the similarity of the samples on the basis of the joint chemical study of polyphenolic composition and volatile profile, the data matrix was subjected to a hierarchical agglomerative cluster analysis of cases. The squared Euclidean distance as the metric and the Ward method as the amalgamation rule were used. The dendrogram obtained is shown in Fig. 1. As can be seen, a cluster was formed according to the highest amounts of fiber (5 and 10 g/L) for orange fiber what demonstrated that the samples with high concentration of orange fiber added were similar between them, regardless the storage conditions employed. Another cluster comprised those samples with the lowest levels of fiber (0, 0.1, 0.5 and 1 g/L) no matter the type of fiber added, so when the quantity of the added fiber was lower, it could be the same the type of fiber used. There is also another cluster formed by the lemon fiber samples stored at low temperature/dark conditions together with control fiber samples. So, this kind of samples were more similar to those without addition of any fiber.

The groups obtained demonstrated that the variables could possess sufficient explanatory power for the detection of the type and amount of the fiber employed for the enrichment process and the storage applied. Thus, in order to obtain suitable classification rules for assigning categories of samples, supervised learning pattern recognition methods were applied. A forward stepwise linear discriminant analysis was carried

out for that purpose. This was performed according to the Wilks' lambda statistics in order to choose the descriptors that best distinguish the different classes. A F statistic is computed from the partial λ values, leading to a p level. Only those phenolic and volatile compounds which manifested significant differences in the analysis of variance (Tables 1 and 2) for each studied factor were considered.

The scatterplot of the samples onto the plane defined by the first two discriminant functions for each factor studied (type, amount and storage) is shown in Fig. 2. As can be seen, a clear separation among vinegars enriched or not with citrus fiber, stored under different thermal/luminosity conditions and with different quantities of fiber was obtained. Taking into account the "type" factor, Fig. 2a evidenced a clear differentiation between control vinegars and both enriched-fiber vinegars. According to p -levels and F -values, the final model selected some variables as discriminant functions to differentiate by type of product: naringin and HMF as phenolic compounds and mainly benzenic compounds (4-methyl-2,6-di-*tert*-butylphenol, phenol, *o*-*tert*-butyl phenol and 2,4-bis(dimethylethyl) phenol as volatile compounds ($p < 0.01$). With regard to the "amount" factor, vinegars without fiber addition (control vinegar) and with the highest quantities (5 and 10 mg/L) were clearly differentiated from the rest of the samples, whereas the intermediate contents of fiber were nearly situated but well differentiated (Fig. 2b). Several compounds participated as discrimination functions ($p < 0.01$): among phenolic compounds, naringin and hesperidin, *t*-caftaric acid and HMF, and *p*-hydroxy-benzaldehyde and tyrosol, and mainly benzenic compounds (4-nonyl phenol, eugenol, *o*-*tert*-butyl phenol, phenol and 4-methyl-2,6-di-*tert*-butylphenol) and others such as decanoic acid, 4-terpineol,

Fig. 1 Cluster analysis of the polyphenol and volatile composition. The dendrogram was obtained using the squared Euclidean distance and the Ward method as the amalgamation rule. Codes: *N* Vinegars with orange fiber addition, *L* Vinegars with lemon fiber addition; Fiber additions: 1: 0.1 g/L, 2: 0.5 g/L, 3: 1 g/L, 4: 5 g/L, 5: 10 g/L, *RT* Stored at room temperature (25 °C) under light conditions, *LT* Stored and low temperature (4 °C) under dark conditions, *CO* Control vinegar

Fig. 2 Forward stepwise linear discriminant (LDA) employing as grouping criterion of “type of product” **a.** *C* Control vinegar, *L* Lemon fiber addition, *O* Orange fiber addition), “amount of fiber” **b.** 0: 0 g/L, 1: 0.1 g/L, 2: 0.5 g/L, 3: 1 g/L, 4: 5 g/L, 5: 10 g/L) and “storage” **c.** *RT* Room temperature under light conditions, *LT* Low temperature under dark conditions). Projection of vinegar samples on the discriminant space selecting the first two discriminant functions as axes

Table 3 ANOVA analysis of volatile compounds

Volatile compound	Type	Amount	Storage
<i>Esters and acetates</i>			
β-phenyl propanoic acid ethyl ester	0.887	0.001*	0.540
hexanoic acid ethyl ester	0.982	0.770	0.682
decanoic acid ethyl ester	0.244	0.311	0.278
benzyl acetate	0.002*	0.276	0.002*
methyl salicylate	0.024*	0.186	0.080
2-ethyl phenyl acetate	0.030*	0.211	0.218
2-phenyl acetate	0.013*	0.621	0.439
isobutyl acetate	0.149	0.190	0.000*
ethyl isovalerate	0.104	0.972	0.857
isoamyl acetate	0.165	0.176	0.165
ethyl acetate	0.666	0.995	0.604
<i>Alcohols</i>			
1-(2-methoxyphenyl) ethanol	0.012*	0.491	0.096
2-methyl-1-butanol	0.015*	0.101	0.141
2-phenyl alcohol	0.061	0.419	0.260
isoamyl alcohol	0.463	0.056	0.683
<i>Acids</i>			
butanoic acid	0.311	0.039*	0.011*
2-phenyl propanoic acid	0.890	0.001*	0.533
isobutyric acid	0.003*	0.070	0.001*
isovaleric acid	0.005*	0.314	0.000*
hexanoic acid	0.013*	0.094	0.001*
heptanoic acid	0.899	0.915	0.275
octanoic acid	0.254	0.015*	0.992
nonanoic acid	0.090	0.000*	0.175
decanoic acid	0.752	0.000*	0.034
dodecanoic acid	0.163	0.772	0.194
<i>Terpenes</i>			
β-terpineol	0.176	0.249	0.451
valencene	0.064	0.129	0.574
neronidol	0.209	0.001*	0.567
citronellol	0.502	0.148	0.273
cis-limonene oxide	0.319	0.408	0.341
eucalyptol	0.552	0.770	0.517
4-terpineol	0.404	0.534	0.292
α-terpineol	0.173	0.057	0.037*
<i>Benzenic compounds</i>			
eugenol	0.037*	0.411	0.374
2-ethyl phenol	0.108	0.041*	0.086
4-methyl-2,6-di-tert-butylphenol	0.338	0.000*	0.024*
4-nonyl phenol	0.010*	0.000*	0.246
benzaldehyde	0.035*	0.333	0.000*
phenol	0.879	0.984	0.188
p-ethyl guaiacol	0.012*	0.493	0.096
4-ethyl phenol	0.102	0.036*	0.094
o-tert-butyl phenol	0.657	0.999	0.212
2,4-bis(dimethylethyl) phenol	0.027*	0.000*	0.029*
<i>Furanic compounds</i>			
furfural	0.911	0.773	0.000*
<i>Lactones</i>			

Table 3 (continued)

Volatile compound	Type	Amount	Storage
δ-nonyl valerolactone	0.246	0.000*	0.709
<i>Aldehydes and ketones</i>			
neryl acetone	0.012*	0.008*	0.433
1-(2,3,6-triethylphenyl)- butanone	0.499	0.000*	0.171
mesityl oxide	0.598	0.007*	0.271
2-nonanone	0.399	0.180	0.264
camphor	0.131	0.595	0.269
(+)-carvone	0.073	0.133	0.577
cis-geranyl acetone	0.049*	0.054	0.763
2-phenyl-2-butenal	0.008*	0.522	0.520
1-(2,3,6-trimethylphenyl)-2-butanone	0.481	0.000*	0.069
2,6-dimethyl-4-heptanone	0.421	0.024*	0.111
<i>Miscellaneous</i>			
benzaldehyde α-ethylene	0.007*	0.527	0.545
4-butyl butan-4-olide	0.478	0.480	0.733
acetoneisole	0.614	0.365	0.419
vitispirane	0.202	0.335	0.000*
n-butyl benzene sulfonamide	0.721	0.997	0.387

*Values are statistically significant at $p < 0.05$

ethyl acetate and 1-(2,3,6-trimethylphenyl)-2-butanone as volatile compounds. Finally, the hydroxycinnamic acid derivatives (*t*- and *c*-*p*-coumaric acids and *t*-caftaric acid) and *p*-hydroxy-benzaldehyde, vitispirane and hexanoate ethyl ester were the variables that well discriminated among samples according to the storage conditions ($p < 0.01$) (Fig. 2c). It is spotlighted that esters, alcohols and furanic compounds did not contribute to the separation by any studied factor. Finally, the 100 % of the samples correctly classified in the check process for each studied factor.

Sensory analysis

Due to the optimization of a new agro-alimentary product is conditioned by the acceptability by consumers, a sensory evaluation (descriptive analysis and ranking test) was carried out.

In relation to descriptive analysis, several aromatic and tasting descriptors were evaluated (aroma intensity, pungent and citric aroma; and acidic and citric flavor, respectively), as well as the olfactory and gustatory impression. A structured 9-point scale was used to assess the sensory parameters. Table 4 shows the scores (mean values and standard deviations) for each descriptor after elimination of outliers and confirming the absence of dissenting judges. These data were submitted to ANOVA (Table 4; $p < 0.05$).

In general, type of product and amount of fiber were the most influential factors in the sensory parameters. Vinegars with fiber were better valued than those vinegars without addition, due to the significantly ($p < 0.05$) best values of the olfactory impression and citric flavor of the vinegars enriched

Table 4 Mean values (and standard deviations) for each descriptor and sample. Analysis of variance. The scores for olfactory and gustatory impression were: bad (0), mediocre (2), acceptable (4), good (6), very good (8); and for the several analytical descriptors: not present (0), slight (2), moderate (4), strong (6), and very strong (8)

	Pungent	Citric odor	Aromatic intensity	Olfactory impression	Acid flavor	Citric flavor	Gustatory impression
C0LT	5.3±1.3	2.4±1.5	4.5±1.4	4.4±1.8	4.5±1.3	2.2±1.6	4.6±1.5
C0RT	5.3±1.3	1.9±1.3	4.7±1.8	3.9±2.0	5.0±1.4	1.6±1.4	4.4±1.8
L1LT	5.6±1.1	2.7±1.0	5.0±1.6	4.7±1.4	4.7±1.2	2.2±1.5	4.8±1.3
L2LT	5.0±1.5	2.4±1.0	4.1±1.2	4.3±1.2	4.6±1.4	2.2±1.5	4.6±1.3
L3LT	5.4±1.2	3.0±1.0	4.8±1.4	5.0±1.5	4.3±1.1	2.4±1.5	5.1±1.2
L4LT	5.5±1.2	3.2±1.2	4.8±1.6	5.4±1.5	4.6±1.2	2.3±1.6	5.3±1.5
L5LT	5.9±1.2	3.7±1.4	5.4±1.4	5.2±1.2	5.1±1.1	2.7±1.6	5.4±1.0
L1RT	5.4±1.4	3.0±1.0	4.8±1.9	5.4±1.6	4.3±1.1	2.1±1.6	5.1±1.6
L2RT	5.5±1.7	3.7±1.4	5.2±1.9	5.6±1.9	4.8±0.8	2.5±1.9	4.9±1.5
L3RT	4.9±1.5	2.8±1.7	4.4±1.4	4.9±1.3	4.5±1.1	2.3±1.9	5.0±1.5
L4RT	5.2±1.4	3.2±0.9	5.0±1.6	4.8±1.3	4.3±0.9	2.1±1.3	5.0±1.4
L5RT	5.2±1.5	3.8±1.1	5.2±1.5	4.9±1.4	4.5±0.9	2.7±1.1	5.1±1.2
O1LT	5.2±1.4	3.1±1.6	5.0±1.9	4.7±1.4	4.4±1.0	2.6±1.8	4.4±1.3
O2LT	5.0±1.3	3.2±1.3	4.8±1.7	4.9±1.6	4.4±1.2	2.8±1.8	4.5±1.3
O3LT	5.2±1.2	3.6±1.3	5.1±1.7	5.2±1.4	4.5±0.9	3.3±1.6	5.2±1.4
O4LT	5.1±1.4	3.9±1.2	5.0±1.9	5.1±1.6	4.2±0.8	3.2±1.2	5.2±1.6
O5LT	5.6±1.2	4.1±1.3	5.7±1.7	5.7±1.6	4.2±0.9	3.4±1.1	5.8±1.3
O1RT	5.4±1.6	1.8±0.9	4.3±1.9	4.4±1.4	4.8±1.2	2.0±1.0	4.5±1.3
O2RT	5.2±0.9	2.1±0.9	4.4±1.3	4.2±0.8	4.2±0.7	2.0±1.3	4.9±1.3
O3RT	4.8±1.1	3.1±0.9	4.3±1.6	5.0±1.8	4.5±0.9	2.4±1.4	5.1±1.2
O4RT	5.2±1.0	4.3±1.8	4.7±1.2	5.2±1.5	4.8±1.1	3.2±1.8	5.6±1.7
O5RT	4.8±1.5	4.2±1.9	4.6±1.2	5.0±1.4	4.9±1.1	3.5±1.9	5.3±1.4
ANOVA							
Type	0.1479	0.1157	0.6567	0.0309*	0.3105	0.0111*	0.1454
Amount	0.5651	0.0044*	0.2177	0.0725	0.6300	0.0478*	0.0009*
Storage	0.1825	0.6813	0.1949	0.5538	0.4346	0.2475	0.9602

*Values are statistically significant at $p < 0.05$

with orange fiber (ANOVA “type” factor). The significantly ($p < 0.05$) highest scores of both citric odor and flavor (LRT, $p = 0.0173$ and $p = 0.0000$; ORT, $p = 0.0643$ for the latter) and gustatory impression (OLT, $p = 0.0264$) of some vinegars made remarkable influenced the amount of fiber added to the vinegars (ANOVA “amount” factor). In fact, the attributes directly correlated with olfactory and gustatory impressions were citric odor and flavor, respectively ($r^2 > 0.79$ and 0.63 ; data not shown), which means that the preference of the vinegars is mainly based on these descriptors. For all these parameters, samples were best valued as the content of fiber increased. Concerning the influence of temperature/luminosity, judges did not detected significant ($p < 0.05$) differences in any sensory parameter (Table 4) (ANOVA “storage” factor).

In order to check the volatile compounds which mostly participated in the most influential sensory attributes, a correlation study was carried out (Table 5). As can be seen, the volatile compounds that highly correlated ($p < 0.05$; $r > 0.05$) with citric odour and flavour, and olfactory and gustatory

impressions were virtually all terpenes (such as β -terpineol, valencene, nerolidol and α -terpineol) and aldehydes and ketones derived from them (neryl acetone and *cis*-geranyl acetone), as well as lactones and some acids and benzenic compounds. The rest of the volatile compounds, most of them esters, alcohols and furanic compounds, did not evidenced any significant correlation with the sensory attributes.

Finally, a high sensory acceptability of fiber-enriched vinegars was confirmed by a ranking test by global impression (gustatory and olfactory). In each session, the assessors were asked to order the vinegar samples. According to the Friedman test, the calculated *F*-value was higher than the corresponding tabulated *F*-value (9–10 judges; assumed error of 5 %), which indicates a significant statistical difference (ISO 2006a) (calculated *F*-value/tabulated *F*-value: LRT, 18.24/10.81; OLT, 11.01/10.91; ORT, 15.94/10.83). In general, as it was observed in the descriptive analysis (Table 4), judges preferred vinegars with fiber, placing vinegars without addition of fiber in the last positions (data not shown). In general,

Table 5 Correlation coefficients between the volatile compounds and sensory parameters (Pearson correlation coefficients)

	Correlation study (<i>p</i> -value)			
	Citric odor	Citric flavor	Olfactory impression	Gustatory impression
<i>Esters and acetates</i>				
β-phenyl propanoic acid ethyl ester	−0.632*	−0.604*	−0.479*	−0.623*
hexanoic acid ethyl ester	0.178	0.139	0.344	0.426*
decanoic acid ethyl ester	0.337	0.432	0.366	0.463*
benzyl acetate	−0.034	0.009	−0.053	0.007
methyl salicylate	−0.103	−0.046	−0.072	−0.119
2-ethyl phenyl acetate	−0.119	−0.059	−0.077	−0.096
2-phenyl acetate	0.128	0.193	0.010	0.200
isobutyl acetate	0.151	0.005	0.098	0.107
ethyl isovalerate	0.145	−0.070	0.259	−0.050
isoamyl acetate	0.408	0.325	0.124	0.192
ethyl acetate	−0.189	−0.126	−0.257	−0.188
<i>Alcohols</i>				
1-(2-methoxyphenyl) ethanol	−0.123	0.087	−0.128	−0.113
2-methyl-1-butanol	0.599*	0.687*	0.513*	0.675*
2-phenyl alcohol	−0.025	0.001	0.019	0.106
isoamyl alcohol	−0.003	−0.107	0.101	0.102
<i>Acids</i>				
butanoic acid	−0.231	−0.262	−0.359	−0.234
2-phenyl propanoic acid	−0.631*	−0.604*	−0.478*	−0.623*
isobutyric acid	0.032	0.090	−0.109	−0.053
isovaleric acid	0.086	0.066	0.017	0.062
hexanoic acid	−0.064	−0.065	−0.089	−0.129
heptanoic acid	−0.075	−0.083	−0.164	−0.108
octanoic acid	−0.415	−0.354	−0.235	−0.329
nonanoic acid	−0.506*	−0.409	−0.300	−0.472*
decanoic acid	−0.705*	−0.581*	−0.466*	−0.703*
dodecanoic acid	0.245	0.390	0.269	0.281
<i>Terpenes</i>				
β-terpineol	0.465*	0.528*	0.091	0.418
valencene	0.496*	0.599*	0.184	0.401
neronidol	−0.546*	−0.437*	−0.367	−0.511*
citronellol	−0.712*	−0.573*	−0.551*	−0.528*
cis-limonene oxide	0.285	0.372	0.392	0.454*
eucalyptol	−0.327	−0.262	−0.278	−0.039
4-terpineol	−0.178	−0.248	−0.369	−0.178
α-terpineol	0.559*	0.522	0.134	0.452*
<i>Benzenic compounds</i>				
eugenol	−0.588*	−0.721*	−0.488*	−0.437*
2-ethyl phenol	−0.252	−0.229	−0.064	−0.206
4-methyl-2,6-di- <i>tert</i> -butylphenol	−0.626*	−0.467*	−0.583*	−0.794*
4-nonyl phenol	−0.737*	−0.680*	−0.581*	−0.750*
benzaldehyde	0.098	−0.006	0.112	0.062
phenol	−0.150	−0.091	−0.109	−0.063
<i>p</i> -ethyl guaiacol	−0.123	0.087	−0.129	−0.112
4-ethyl phenol	−0.274	−0.245	−0.084	−0.227
<i>o</i> - <i>tert</i> -butyl phenol	−0.388	−0.448*	−0.484*	−0.384

Table 5 (continued)

	Correlation study (<i>p</i> -value)			
	Citric odor	Citric flavor	Olfactory impression	Gustatory impression
2,4-bis(dimethylethyl) phenol	−0.745*	−0.693*	−0.570*	−0.769*
<i>Furanic compounds</i>				
furfural	0.040	−0.135	0.181	0.116
<i>Lactones</i>				
δ-nonyl valerolactone	−0.706*	−0.667*	−0.469*	−0.663*
<i>Aldehydes and ketones</i>				
neryl acetone	0.673*	0.776*	0.430*	0.643*
1-(2,3,6-triethylphenyl)- butanone	−0.660*	−0.605*	−0.436*	−0.646*
mesityl oxide	−0.463*	−0.492*	−0.252	−0.419
2-nonanone	−0.426*	−0.520*	−0.382	−0.369
camphor	0.028	−0.173	−0.100	−0.023
(+)-carvone	0.498*	0.597*	0.175	0.397
cis-geranyl acetone	0.663*	0.733*	0.486*	0.658*
2-phenyl-2-butenal	0.138	0.256	−0.035	0.196
1-(2,3,6-trimethylphenyl)-2-butanone	−0.695*	−0.623*	−0.490*	−0.679*
2,6-dimethyl-4-heptanone	0.044	−0.079	0.108	−0.132
<i>Miscellaneous</i>				
benzaldehyde α-ethylene	0.151	0.273	−0.023	0.202
4-butyl butan-4-olide	−0.278	−0.247	−0.175	−0.175
acetoneisole	0.420	0.507	0.208	0.463
vitispirane	−0.160	−0.052	−0.063	−0.209
<i>n</i> -butyl benzene sulfonamide	−0.186	−0.110	−0.131	−0.100

*Values are statistically significant at $p < 0.05$

the highest doses of fiber were preferred for vinegars with orange fiber (1, 5 and 10 g/L), whereas the preferred amounts for vinegars enriched with lemon fiber were the lowest (0.1, 0.5 and 1 g/L). The conservation under low temperature/dark conditions provoked that the preference of the quantity of lemon fiber added to vinegars was insignificant (calculated *F*-value/tabulated *F*-value: LLT, 3.37/10.90).

Conclusions

The results obtained indicate that the enrichment with citrus fiber enhanced the bioactive profile of Sherry vinegars (polyphenolic and volatile compounds). Fiber from orange provided higher content of volatile compounds and lower of polyphenols, contrarily to that derived from lemon. Storage conditions did not exert a significant and appreciable effect in the chemical profile. From a sensory point of view, fiber-enriched vinegars were significantly preferred, but the dose of fiber greatly influenced on the acceptability according to the fiber source. Any vinegar maker company could be brought the establishment of this new agro-alimentary product to fruition because, in addition of contributing with the added value of

being a good source of fiber claim, it will offer diversification in the market's product line. Although it is true that the amount of vinegar intake in the diet is limited and so the benefits on health, this new product still could have some beneficial effects on the final consumers.

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